REMARKS

Claims 1-3, 7-19, 21, 24-33 and 57-66 are pending in the application.

Claims 1-3, 11, 13, 16, 18-19, 27, 29, 32 and 57-64 are rejected as unpatentable over OHASHI et al. 6,376,345 in view of NGO et al. 6,596,631. Claims 8-10, 14, 24-26 and 30 are rejected as unpatentable over OHASHI et al. in view of NGO et al. and further in view of LAWSON 4,978,756. Claims 7 and 21 are rejected as unpatentable over OHASHI et al. in view of NGO et al. and further in view of applicants' disclosed prior art. Claims 12, 15, 17, 28, 31 and 33 are rejected as unpatentable over OHASHI et al. in view of NGO et al. These rejections are respectfully traversed.

The only section under which the NGO et al. patent could be prior art is 35 USC §102(e). The §102(e) date of NGO et al. is its July 26, 2000 U.S. filing date. Applicants claim priority to Japanese Application No. 11-329324 filed on November 19, 1999 which antedates NGO et al.'s earliest 102(e) date.

Applicants submit herewith a verified English translation of the Japanese priority document to perfect the claim to priority and remove NGO et al. as a prior art reference.

Each rejection applies the NGO et al. reference. As such reference is unavailable as prior art, none of the rejections can be maintained.

In view of the foregoing remarks, it is believed that the present application is in condition for allowance. Reconsideration and allowance are respectfully requested.

The Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 25-0120 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17.

Respectfully submitted,

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Appendix:

An Appendix includes the following item:

- a verified English translation of Japanese Appln. No. 11-329324

VERIFICATION OF THE TRANSLATION

I, the below-named Chartered Patent Attorney of Tokyo Japan having an office at an address stated below, hereby declare that :

I am knowledgeable in the English and Japanese languages, and I believe that the attached English translation of the Japanese Patent Application No. 11-329324 filed on November 19, 1999 is a true and complete translation of said application.

I also hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date : October 20, 2004

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(English Translation)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application : November 19, 1999
Application Number : Japanese Patent Application No. 11-329324
Applicant : NEC Corporation

Commissioner,
Patent Office

[Kind of Document]	Application for Patent
[Reference Number]	74112071
[Date of Submission]	November 19, 1999
[Addressee]	The Commissioner of the Patent Office
[IPC]	H01L 21/304
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[Account No.]	000435
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[Kind of Document]	Specification 1 copy
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(English Translation)

[Document Name] Specification

[Title of the Invention] Method of manufacturing semiconductor wafer and semiconductor device

[Scope of Claims]

[Claim 1]

A method of manufacturing a semiconductor device, wherein before a copper-diffusion stopper insulating film is formed on a surface of a semiconductor substrate, of which copper or a copper alloy has been exposed, said surface of said semiconductor substrate is subjected to anti-corrosion treatment with a solution to which an anti-corrosive agent is added.

[Claim 2]

The method of manufacturing the semiconductor device as claimed in claim 1, wherein said semiconductor substrate, of which copper or a copper alloy has been exposed is a semiconductor substrate in which a metal interconnection comprising copper or a copper alloy is formed by a damascene method.

[Claim 3]

The method of manufacturing the semiconductor device as claimed in claim 1 or 2, wherein said anti-corrosion treatment is carried out during a cleaning process after said copper or copper alloy is subjected to chemical mechanical polishing (CMP).

[Claim 4]

The method of manufacturing the semiconductor device as claimed any one in claim 1, 2, or 3, wherein said anti-corrosion treatment is carried out immediately after cleaning treated with a cleaning solution for removing metal contamination,

[Claim 5]

The method of manufacturing the semiconductor device as claimed in claim 1, 2 or 3, wherein said anti-corrosion treatment is carried out at the same time as cleaning for removing metal contamination with a cleaning solution to which an anti-corrosive agent is added.

[Claim 6]

The method of manufacturing the semiconductor device as claimed in claim 4 or 5, wherein said cleaning solution is a carboxylic acid based cleaning solution.

[Claim 7]

The method of manufacturing the semiconductor device as claimed any one in claims 1 to 6, wherein said anti-corrosive agent comprises at least one of four-membered hetero-cyclic compounds having two nitrogen atoms, or five-membered hetero-cyclic compounds having three nitrogen atoms, or six-membered hetero-cyclic compounds having three nitrogen atoms, or derivatives thereof, or two or more of these mixtures.

[Claim 8]

The method of manufacturing the semiconductor device as claimed in claim 7, wherein said four-membered hetero-cyclic compounds are indazole or derivatives thereof.

[Claim 9]

The method of manufacturing the semiconductor device as claimed in claim 7, wherein said five-membered hetero-cyclic compounds are benzotriazole, o-tolyltriazole, m-tolyltriazole, p-tolyltriazole, carboxybenzotriazole, 1-hydroxybenzotriazole, nitrobenzotriazole, or dihydroxypropylbenzotriazole.

[Claim 10]

The method of manufacturing the semiconductor device as claimed any one in claims 1 to 9, wherein said anti-corrosive agent has an additive rate of 1 ppm to 5%.

[Claim 11]

The method of manufacturing the semiconductor device as claimed any one in claims 1 to 6, wherein said anti-corrosive agent comprises at least one of compounds having aromatic benzene-rings or derivatives thereof, or two or more of these mixtures.

[Claim 12]

The method of manufacturing the semiconductor device as claimed in claim 11, wherein said compounds having aromatic benzene-rings are gallic acid or tannic acid.

[Claim 13]

The method of manufacturing the semiconductor device as claimed in claim 12, wherein said gallic acid or tannic acid has an additive rate of 0.01 to 5%.

[Claim 14]

The method of manufacturing the semiconductor device as claimed

any one in claims 1 to 13, wherein said copper-diffusion stopper insulating film is Si_3N_4 or SiON.

[Claim 15]

A method of manufacturing a semiconductor wafer having a metal interconnection comprising copper or a copper alloy by a damascene method, the method comprising the steps of:

treating metal with use of CMP to form said metal interconnection; and

carrying out anti-corrosion treatment of a surface of said metal interconnection with a solution to which an anti-corrosive agent is added during cleaning after said CMP treatment.

[Claim 16]

The method of manufacturing the semiconductor wafer as claimed in claim 15, wherein said anti-corrosion treatment is carried out immediately after cleaning for removing metal contamination.

[Claim 17]

The method of manufacturing the semiconductor wafer as claimed in claim 16, wherein said anti-corrosion treatment is carried out at the same time as cleaning for removing metal contamination with a cleaning solution to which an anti-corrosive agent is added.

[Claim 18]

The method of manufacturing the semiconductor wafer as claimed in claim 17, wherein said cleaning solution is a carboxylic acid based cleaning solution.

[Claim 19]

The method of manufacturing the semiconductor wafer as claimed any one in claims 15 to 18, wherein said anti-corrosive agent comprises at least one of four-membered hetero-cyclic compounds having two nitrogen atoms, or five-membered hetero-cyclic compounds having three nitrogen atoms, or six-membered hetero-cyclic compounds having three nitrogen atoms, or derivatives thereof, or two or more of these mixtures.

[Claim 20]

The method of manufacturing the semiconductor wafer as claimed in claim 19, wherein said four-membered hetero-cyclic compounds are indazole or derivatives thereof.

[Claim 21]

The method of manufacturing the semiconductor wafer as claimed in claim 19, wherein said five-membered hetero-cyclic compounds are benzotriazole, o-tolyltriazole, m-tolyltriazole, p-tolyltriazole, carboxybenzotriazole, 1-hydroxybenzotriazole, nitrobenzotriazole, or dihydroxypropylbenzotriazole.

[Claim 22]

The method of manufacturing the semiconductor wafer as claimed any one in claims 15 to 21, wherein said anti-corrosive agent has an additive rate of 1 ppm to 5%.

[Claim 23]

The method of manufacturing the semiconductor wafer as claimed any one in claims 15 to 18, wherein said anti-corrosive agent comprises at least one of compounds having aromatic benzene-rings or derivatives thereof, or two or more of these mixtures.

[Claim 24]

The method of manufacturing the semiconductor device as claimed in claim 23, wherein said compounds having aromatic benzene-rings are gallic acid or tannic acid.

[Claim 25]

The method of manufacturing the semiconductor wafer as claimed in claim 24, wherein said gallic acid or tannic acid has an additive rate of 0.01 to 5%.

[Claim 26]

The semiconductor wafer formed by a method as claimed any one in claims 15 to 25, wherein an anti-corrosive film comprising a compound of copper and said anti-corrosive agent is formed on a surface of said metal interconnection.

[Claim 27]

The semiconductor wafer as claimed in claim 26, wherein said compound is copper-BTA which is a compound of copper and benzotriazole (BTA).

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a method of manufacturing a semiconductor wafer, and in particular, to a method of manufacturing a

semiconductor wafer including a cleaning process of a semiconductor device, of which copper or a copper alloy has been exposed. The present invention further relates to a method of manufacturing a semiconductor device using such a semiconductor wafer.

[0002]

[Background Art]

In recent years, as a material for a metal interconnection in a semiconductor device, copper or a copper alloy (hereinafter, referred to as Cu) containing not less than 80% of copper is increasingly being used. An interconnection using a Cu is generally formed by a damascene method. FIG. 7 shows processes of a method of manufacturing a conventional semiconductor device which forms a damascene Cu-interconnection. In addition, FIG. 8A, FIG. 8B and FIG. 8C show a partial cross section of a semiconductor wafer in the manufacturing processes, respectively

[0003]

As shown in FIG. 8A, an insulating film 12 such as a silicon dioxide film (hereinafter, referred to as SiO_2) is formed on a semiconductor substrate 10, or an inter-layer film not shown, and the interconnection is formed in part of the insulating film. A barrier metal layer 14 such as Ta or TaN is formed inside an interconnection groove. A Cu-seed layer 15 is formed by a sputtering method or a CVD method, and a Cu 16 is attached thereon by an electroplating method.

[0004]

The above-mentioned semiconductor wafer 1 is loaded into cleaning apparatus, so that in a Cu-CMP process 20 shown in FIG. 7, the Cu is left in the interconnection groove to remove the CU in the upper portion, whereby a Cu-interconnection 17 is formed as shown FIG. 8B.

[0005]

Next, in a scrub cleaning process 22, particle contamination is removed with cleaning treatment such as a brush scrub. Subsequently, in a spin cleaning process 24, metal contamination is removed with a cleaning solution such as a carboxylic based cleaning solution (an oxalic acid solution and the like). Moreover, in a spin-rinse + dry process 26, the semiconductor wafer 1 is rinsed and dried, and then unloaded from the cleaning apparatus.

[0006]

Subsequently, in a film forming process 28, the semiconductor

wafer 1 is fed to film forming apparatus in order to form a Cu-diffusion stopper insulating film such as a silicon nitride film (hereinafter, referred to as Si_3N_4 film) or SiON on a surface thereof, whereby, for example, an Si_3N_4 film 18 is formed on the surface of the semiconductor wafer, as shown in FIG. 8C. An inter-layer film 19 such as SiO_2 is then formed.

[0007]

In the manufacturing processes described above, the semiconductor wafer is exposed to the atmosphere during a time period from when the semiconductor wafer is cleaned after CMP and removed from cleaning apparatus until it is loaded into a vacuum chamber of Si_3N_4 film forming apparatus. This exposure time depends on a waiting time until the semiconductor wafer is loaded into the film forming apparatus. However, it is predicted to wait in units of day in actual manufacturing sites.

[0008]

[Problems to be Solved by the Invention]

The above-mentioned method of manufacturing the conventional semiconductor device gave rise to a problem that adhesion of an interface between a Cu surface and the Cu-diffusion stopper insulating film is deteriorated when manufacturing the Cu-diffusion stopper insulating film on the semiconductor wafer exposed to the atmosphere.

[0009]

Additionally, while manufacturing the Cu-diffusion stopper insulating film, or in the subsequent processes, a hillock was sometimes formed on a Cu-interconnection surface when a film stress was applied or heating treatment was carried out.

[0010]

In case of poor adhesion in the interface between the Cu and the Cu-diffusion stopper insulating film described above, the Cu enters into a gap between a Cu-interconnection and the Cu-diffusion stopper insulating film by a current stress applied when the current flows through the Cu-interconnection, to cause a short circuit with an adjacent interconnection, resulting in a problem with a decrease in the reliability of semiconductor devices. In addition, formation of the hillock on the Cu-interconnection surface causes the decreased reliability of semiconductor devices.

[0011]

The inventors of the present application found out the following

facts in an attempt to locate the cause. Namely, when a wafer is exposed to the atmosphere after cleaning subsequent to CMP, and before manufacturing the Cu-diffusion stopper insulating film, the Cu-interconnection surface is oxidized to thereby form CuOx (hereinafter, referred to as CuO), leading to poor adhesion. In addition, the CuO is nonuniformly formed on the Cu-interconnection surface. In other words, if a location where the CuO is formed and a location where the CuO is not formed are distributed and exist, the hillock may be formed.

[0012]

Accordingly, the inventors of the present application came to realize that it is good to prevent any oxidation of the Cu-interconnection surface and thus formation of the CuO on the Cu-interconnection surface even if the semiconductor wafer is exposed to the atmosphere before the Cu-diffusion stopper insulating film is formed.

[0013]

It is, therefore, an object of the present invention to provide a semiconductor wafer free from any oxidation of a Cu-interconnection surface, even if the semiconductor wafer is exposed to the atmosphere.

[0014]

It is another object of the present invention to provide a method of manufacturing such a semiconductor wafer.

[0015]

It is still another object of the present invention to provide a method of manufacturing a semiconductor device which solves a problem of poor adhesion with a Cu-diffusion stopper insulating film.

[0016]

It is yet another object of the present invention to provide a method of manufacturing a semiconductor device which prevents formation of a hillock.

[0017]

[Means for Solving the Problems]

In accordance with a method of manufacturing the semiconductor wafer of the present invention, in a cleaning treatment process after Cu-CMP for manufacturing a damascene Cu-interconnection, an anti-corrosive film comprising a compound of Cu and an anti-corrosive agent is formed by carrying out cleaning treatment with a solution to which the anti-corrosive

agent is added. The presence of this film may serve prevention from any oxidation of a Cu-interconnection surface. Therefore, even if the semiconductor wafer is exposed to the atmosphere before the subsequent process of manufacturing a Cu-diffusion stopper insulating film, the Cu-interconnection surface is prevented from any oxidation, thus resulting in excellent adhesion of the formed Cu-diffusion stopper insulating film. In addition, a CuO film is not formed, whereby a hillock is never formed on the Cu-interconnection surface by a heat treatment process.

[0018]

To suppress Cu-diffusion from a Cu-interconnection, an insulating film coated on the interconnection includes Si_3N_4, SiON, and SiO_2.

[0019]

Benzotriazole (BTA) is known as a typical Cu anti-corrosive agent. A technology using BTA in manufacturing the interconnection of the semiconductor device has already been disclosed in Japanese Unexamined Patent Publication No. 08(1996)-64594 "WIRING FORMATION METHOD", and Japanese Unexamined Patent Publication No. 11(1999)-40526 "WIRING FORMATION METHOD AND MANUFACTURE OF SEMICONDUCTOR DEVICE".
These technologies allow BTA to come into contact with a Cu surface at the same time as CMP or immediately after the CMP, thereby achieving anti-corrosion effects.

[0020]

In contrast with these conventional technologies, the present invention is characterized in that in the cleaning treatment process after the CMP, a metal-interconnection surface is treated with a solution to which the anti-corrosive agent is added.

[0021]

Moreover, the present inventors confirmed that the anti-corrosive agent comprising at least one of four-membered hetero-cyclic compounds having two nitrogen atoms, or five-membered hetero-cyclic compounds having three nitrogen atoms, or six-membered hetero-cyclic compounds having three nitrogen atoms, or derivatives thereof, or two or more of these mixtures is effective as the anti-corrosive agent.

[0022]

The five-membered hetero-cyclic compounds having three nitrogen

atoms are triazole based compounds, whereas the six-membered hetero-cyclic compounds having three nitrogen atoms are triazine based compounds. The triazole based compounds may include benzotriazole, o-tolyltriazole, m-tolyltriazole, p-tolyltriazole, carboxybenzotriazole, 1-hydroxybenzotriazole, nitrobenzotriazole, and dihydroxypropylbenzotriazole, except for the above-mentioned benzotriazole. Moreover, the derivatives of benzotriazole are, for example, Irgamet series commercially available from Chiba Specialty Chemicals. More specifically, Irgamet 42 (2,2' -[[methyl-1H-benzotriazole-1-yl]methyl]imino]bis-ethanol) and the like are preferably used as well.

[0023]

It was confirmed that these anti-corrosive agents exert effects at an additive rate of not less than 1 ppm. In addition, the maximum additive rate is preferably made 5% in view of the environmental problem and the solubility.

[0024]

Gallic acid, tannic acid, and the like of compounds having aromatic benzene-rings, oxidation inhibitors, may also be used as other anti-corrosive agents. These additive rates are preferably made 0.01 to 5% in the same light as the anti-corrosive agent like BTA.

[0025]

It is necessary that the treatment with a solution to which the above anti-corrosive agents are added be carried out in cleaning apparatus after the CMP as a consecutive sequence. The reason is that, for example, anti-corrosion treatment is carried out subsequent to a spin cleaning for removing metal contamination, but that a discontinuity between these processes could form CuO on a metal surface.

[0026]

In order to avoid such a problem, an anti-corrosive solution may be mixed with a cleaning solution to carry out the cleaning treatment and the anti-corrosion treatment at the same time.

[0027]

[The Embodiment of the Invention]

[0028]

[The First Embodiment]

FIG. 1 is a process chart showing a method of manufacturing a semiconductor device according to a first embodiment of the present

invention. The difference from the conventional manufacturing method shown in FIG. 7 is in that an anti-corrosion treatment process 25 is added. Therefore, in FIG. 1, the same processes as those of FIG. 7 are shown in the same reference numbers as those of FIG. 7. Note that the semiconductor device formed in this embodiment is rendered the same one as that described in FIG. 8.

[0029]

In a Cu-CMP process 20, a Cu (a Cu-seed layer 15 or a plated Cu 16) and a barrier metal layer 14 on an insulating film 12 formed in a semiconductor wafer 1 with the structure of FIG. 8A are polished and removed with use of CMP to thereby form a Cu-interconnection 17 (refer to FIG. 8B). Note that it is known that an anti-corrosive agent such as BTA is added to CMP slurry to prevent oxidation of a Cu surface.

[0030]

When the Cu-CMP is carried out, a semiconductor wafer surface is contaminated with adhesion of particles, metal, slurry, and the like such as polishing grains and polishing waste.

[0031]

In a scrub cleaning process 22, a brush is rotated with supply of a cleaning solution such as electrolytic ion water or dissolved hydrogen water to a rotating brush to remove particle contamination.

[0032]

Next, in a spin cleaning process 24, the semiconductor wafer is rotated with supply of a carboxylic acid based cleaning solution comprising a 0.03% solution of oxalic acid for 10 seconds to remove metal contamination, that is, CuO from the surface thereof, and is then rinsed with pure water. Note that the concentration of oxalic acid in the solution may be in the range of 0.01 to 1% solutions, and that time for supplying the solution may be in the range of 10 to 30 seconds. Besides oxalic acid, organic acids such as citric acid may be used.

[0033]

Next, in an anti-corrosion treatment process 25, a wafer surface is treated for anti-corrosion of the Cu-interconnection 17. A BTA solution to which 1% of BTA was added, was prepared as an anti-corrosive solution, and the semiconductor wafer 1 was rotated with supply of the BTA solution to the wafer surface at a flow rate of 1 liter/min. for 10 seconds to carry out the anti-

corrosion of a Cu-film.

[0034]

In the subsequent spin-rinse + dry process 26, the semiconductor wafer 1 was rinsed with pure water for 15 seconds and then dried.

[0035]

Moreover, the present inventors confirmed that the anti-corrosive agent comprising at least one of four-membered hetero-cyclic compounds having two nitrogen atoms, or five-membered hetero-cyclic compounds having three nitrogen atoms, or six-membered hetero-cyclic compounds having three nitrogen atoms, or derivatives thereof, or two or more mixtures of these compounds is effective as the anti-corrosive agent.

[0036]

The five-membered hetero-cyclic compounds having three nitrogen atoms are triazole based compounds, whereas the six-membered hetero-cyclic compounds having three nitrogen atoms are triazine based compounds. The triazole based compounds may include o-tolyltriazole, m- tolyltriazole, p-tolyltriazole, carboxybenzotriazole, 1-hydroxybenzotriazole, nitrobenzotriazole, and dihydroxypropylbenzotriazole except for the above-mentioned benzotriazole. Moreover, the derivatives of benzotriazole are, for example, Irgamet series commercially available from Chiba Specialty Chemicals. More specifically, Irgamet 42 (2,2'-[[methyl-1H-benzotriazole-1-yl]methyl]imino]bis-ethanol) and the like are preferably used as well.

[0037]

It was confirmed that these anti-corrosive agents exert effects at an additive rate of not less than 1 ppm%. In addition, it is preferable to make the maximum additive rate of BTA and the like 5% in view of the environmental problem and the solubility.

[0038]

Gallic acid and tannic acid of compounds having aromatic benzene-rings, oxidation inhibitors, may be used as other anti-corrosive agents. These additive rates are preferably made 0.01 to 5% in the same light as the anti-corrosive agent like BTA.

[0039]

The thus obtained semiconductor wafer was exposed to the atmosphere during a time period of a few hours through a few days. Subsequently, in a film forming process 28, an Si_3N_4 film 18 was treated by a

CVD method at 400ºC for 10 to 15 seconds to form the Si_3N_4 film 18 having a film thickness of 50 nm, on which an inter-layer film 19 having a film thickness of 1.1 μm was formed by treating a plasma oxide film at 400ºC for 70 seconds (refer to FIG. 8C).

[0040]

As a comparative example, a semiconductor wafer free from the anti-corrosion treatment was formed in the above-mentioned process, and was similarly exposed to the atmosphere during the time period of a few hours through a few days before the Si_3N_4 film was formed.

[0041]

In the manufacturing processes according to the present embodiments and in the manufacturing processes for comparative examples, the surface was observed to examine a state where the CuO as the oxide film and Cu-BTA as an anti-corrosive film were formed, with use of TOF-SIMS (Time of Flight-Secondary Ion Mass Spectroscopy), a type of a chemical state analyzer. The TOF-SIMS is a device which analyzes a chemical state of a sample surface without having to break chemical bonds of the sample surface by irradiating a primary ion on the sample (semiconductor wafer 1) surface in pulse to cause generation of a secondary ion, and counting the mass and the ion number of this secondary ion.

[0042]

For the Cu-BTA and the CuO, the wafer in a state after the spin-rinse + dry process 26 and before the Si_3N_4 film forming process 28 was examined. The results are shown in FIG. 2A to FIG. 4. FIG. 2A and FIG. 2B show the CuO respectively, FIG.3 shows organic substances and ionic substances present in the atmosphere, and FIG. 4 shows measurement results of TOF-SIMS on the Cu-BTA. In FIG. 2A and FIG. 4, the ordinate axis represents intensity (intensity when the number of ion count is indicated in arbitrary unit (AU)), and the abscissa axis represents the mass number.

[0043]

FIG. 2A is a graph illustrative of measurement of CuO intensity with use of TOF-SIMS after the semiconductor wafer 1 subjected to the spin-rinse + dry (process 26 in FIG. 1) is exposed to the atmosphere for seven days. As seen from the measurement results of FIG. 2A, in the semiconductor wafer subjected to the anti-corrosion treatment (BTA treatment) according to the present invention, formation of the CuO is suppressed. Additionally, as

shown in the comparative example (no BTA treatment), even the semiconductor wafer 1 subjected to the CMP in the slurry containing BTA has less anti-corrosive effects.

[0044]

FIG. 2B is a graph illustrative of a relationship between the number of days exposed to the atmosphere and the CuO intensity after the semiconductor wafer 1 is subjected to the spin-rinse + dry (process 26 in FIG. 1). As shown in FIG. 2B, the comparative example (no BTA treatment) reveals that the CuO intensity increases along with an increase in the number of exposure days, and that oxidation of the CuO is thus likely to progress. By contrast, the example (BTA treatment) reveals that an increase in the CuO intensity is slow even if the number of exposure days increases, and that oxidation of the CuO is thus unlikely to progress.

[0045]

In addition, FIG. 3 is a graph illustrative of a relationship between the number of days exposed to the atmosphere and organic substance intensity after the semiconductor wafer 1 is subjected to the spin-rinse + dry (process 26 in FIG. 1). Here, the organic substances mean any substances floating in the atmosphere in a clean room, and are presumably any substances generated from a coating material on walls and manufacturing apparatus, or a lubrication agent attached to mobile portions of the manufacturing apparatus.

[0046]

As shown in the comparative example (no BTA treatment) of FIG. 3, it is revealed that even the semiconductor wafer 1 subjected to the CMP in the slurry containing BTA tends to have the organic substances attached, and that the attachment amount of the organic substances significantly increases along with the increase in the number of exposure days.

[0047]

By contrast, the example (BTA treatment) reveals that the increase in the organic substance intensity is slow even if the number of exposure days increases, and that attachment of the organic substances or ionic contaminants harmful in manufacturing the semiconductor wafer 1 may be significantly suppressed.

[0048]

FIG. 4 is a graph illustrative of measurement of Cu-BTA intensity with use of TOF-SIMS after the semiconductor wafer 1 subjected to the spin-

rinse + dry (process 26 in FIG. 1) is exposed to the atmosphere for seven days.
[0049]

As is apparent from the measurement results of FIG. 4, for the semiconductor wafer 1 subjected to the anti-corrosion treatment, the presence of the Cu-BTA as the anti-corrosive film was confirmed. In addition, as shown in the comparative example (no BTA treatment), it is revealed that even the semiconductor wafer 1 subjected to the CMP in the slurry containing BTA has less residual amount of the Cu-BTA. It is further revealed that the Cu-BTA is unlikely to be formed when the CuO is formed on the Cu surface, from a viewpoint combined with the results of FIG. 2.
[0050]

Next, the semiconductor wafer subjected to the anti-corrosion treatment according to the present embodiment and the aforementioned semiconductor wafer formed as a comparative example, were subjected to the spin-rinse + dry process 26, and then exposed to the atmosphere for one day, three days, and seven days, before the Si_3N_4 film was formed, for which an adhesion test of an interface between the Cu and Si_3N_4 was carried out. In this test, adhesive tapes were attached on the Si_3N_4 film in which lines were drawn in a 1 mm-pitch matrix pattern and were peeled therefrom. The number of matrix cells peeled from the wafers in 100 matrix cells was then counted.
[0051]

The above test results are shown in Table 1. As is apparent from the results, the Si_3N_4 film is peeled in any one of the wafers with no BTA treatment. As the time period from when the semiconductor wafer is subjected to the spin-rinse + dry process 26 before it is exposed to the atmosphere until the Si_3N_4 film is formed is prolonged, the number of peeling of the Si_3N_4 film is increased. This reveals the deteriorated adhesion of the interface between the Cu and Si_3N_4. On the other hand, no peeling of the Si_3N_4 film is noted in the wafers with BTA treatment even if a film forming is made over the Si_3N_4 film. This reveals excellent adhesion between the Cu and the Si_3N_4 film.
[0052]
[Table 1]

The number of peeling in an interface between Cu and Si_3N_4

		immediately after	1-day exposure	3-day exposure	7-day exposure
oxalic acid	No BTA treatment	5	10	19	44
	BTA treatment	0	0	0	0

The number of the peeled matrixes in 100 matrix cells (1 mm-pitch)

The number of peeling in an interface between Cu and Si_3N_4 The number of the peeled matrixes in 100 matrix cells(1 mm-pitch)

[0053]

A relationship between BTA concentration and the number of peeled matrix cells of the Si_3N_4 film is shown in Table 2. For a method of an adhesion test, the number of matrix cells in which the Si_3N_4 film was adhered to the adhesive tapes as described above was counted after the semiconductor wafer 1 was soaked in the BTA solutions for each concentration for 10 seconds. As shown in Table 2, no peeling of the Si_3N_4 film is noted in the BTA concentration of 1 ppm to 1%, which proves to be excellent in the adhesion between the Cu and the Si_3N_4 film. The BTA concentration of not less than 1% also produces the same effect as the above-mentioned concentration, but the BTA of not less than 2 to 5% is not dissolved in water.

[0054]

[Table 2]

BTA concentration	the number of peeling
1% (10000 ppm)	0
0.50% (5000 ppm)	0
0.10% (1000 ppm)	0
0.05% (500 ppm)	0
0.01% (100 ppm)	0
0.0050% (50 ppm)	0
0.0005% (5 ppm)	0
0.0001% (1 ppm)	0
0.00005% (0.5 ppm)	4

[0055]

Examples in which a relationship between the presence or absence of the spin cleaning process(oxalic acid treatment) 24 and the anti-corrosion treatment process (BTA treatment), and the number of peeling of the Si_3N_4 films has been tested are shown in Table 3. The semiconductor wafer 1 used for the test employed the semiconductor wafer which was subjected to the spin-rinse + dry 26,and then exposed to the atmosphere for seven days, followed by formation of the Si_3N_4 film.

[0056]

[Table 3]

oxalic acid treatment	absence	absence	presence	presence
BTA treatment	absence	presence	absence	presence
(film forming after a 7-day exposure				
the number of peeling	40	30	44	0

[0057]

From the test results in Table 3, even if the semiconductor wafer 1 in which the metal contamination is not removed(oxalic acid treatment) is subjected to the BTA treatment, then no improvement in the adhesion of the Si_3N_4 film is obtained. In addition, unless even the semiconductor wafer 1 in which the metal contamination is removed is subjected to the BTA treatment, no improvement in the adhesion of the Si_3N_4 film is obtained. This reveals that unless the anti-corrosion treatment is carried out in a state where the Cu surface is cleaned, more specifically, after the CuO or the metal contamination is removed, no effects are produced.

[0058]

Additionally, in place of the BTA solution, a solution which contains 1% gallic acid having effects to prevent oxidation was used as the other anti-corrosive agents to form semiconductor wafers. The semiconductor wafers were then exposed to the atmosphere for one day, three days and seven days respectively, for which sheet resistance of the Cu-interconnection was measured. As a comparison, a rate of variation in the sheet resistance was measured for the semiconductor wafers subjected to the anti-corrosion treatment with a 0.1% BTA solution and with a 1% BTA solution, and the ones not subjected to the anti-corrosion treatment.

[0059]

The measurement results are shown in FIG. 5. For the semiconductor wafers not treated, the variation in the sheet resistance of the

Cu-interconnection is increased as a time period of exposing the semiconductor wafers to the atmosphere is prolonged. However, for the semiconductor wafers treated with the BTA solution and the gallic acid solution, the variation in the sheet resistance is low. This reveals that both the BTA solution and the gallic acid solution are effective in preventing corrosion of the Cu-interconnection and deterioration of the sheet resistance.

[0060]

Additionally, for the semiconductor wafers treated with the BTA solution and the gallic acid solution, it was not confirmed that a hillock is formed even if heat treatment is carried out at 400ºC for 5 minutes at the time of manufacturing the inter-layer film such as the Si_3N_4 film or a silicon oxide film.

[0061]

[The Second Embodiment]

FIG. 6 is a process chart showing a method of manufacturing a semiconductor device according to a second embodiment of the present invention. The difference from the first embodiment is in that BTA is added to an oxalic acid solution in carrying out a spin cleaning for removing metal contamination, instead an anti-corrosion treatment process 25 in FIG. 1 is omitted. FIG. 6 shows the spin cleaning (metal contamination control treatment + anti-corrosion treatment) process in 30. In the other processes, the same processes as those of FIG. 1 are shown in the same reference numbers as those of FIG. 1.

[0062]

In the process 30, the semiconductor wafer was rotated with supply of a solution to which, for example, 0.03% of oxalic acid and 0.5% of BTA were added, and was then spin-rinsed and dried in a process 26. Here, the oxalic acid has a function to remove metal contaminants attached to the semiconductor wafer 1 with use of CMP and a CuO film on the surface thereof. In addition, the BTA has an anti-corrosive function as with the first embodiment. Moreover, the present inventors confirmed that the anti-corrosive agent comprising at least one of four-membered hetero-cyclic compounds having two nitrogen atoms or five- membered hetero-cyclic compounds having three nitrogen atoms or six-membered hetero-cyclic compounds having three nitrogen atoms, or derivatives thereof, or two or more of these compounds is effective as an anti-corrosive agent as well as the

BTA.

[0063]

One example of the four-membered hetero-cyclic compounds is indazole.

[0064]

The five-membered hetero-cyclic compounds having three nitrogen atoms are triazole based compounds, whereas the six-membered hetero-cyclic compounds having three nitrogen atoms are triazine based compounds. The triazole based compounds may include benzotriazole, o-tolyltriazole, m-tolyltriazole, p-tolyltriazole, carboxybenzotriazole, 1-hydroxybenzotriazole, nitrobenzotriazole, and dihydroxypropylbenzotriazole. Moreover, the derivatives of the benzotriazole, for example, Irgamet series commercially available from Chiba Specialty Chemicals. More specifically, Irgamet 42 (2,2'-[[methyl-1H-benzotriazole-1-yl]methyl]imino]bis-ethanol) and the like are preferably used as well.

[0065]

It was confirmed that these anti-corrosive agents exert effects at an additive rate of not less than 1ppm%. In addition, it is preferable to make the maximum additive rate of the BTA and the like 5% in view of the environmental problem and the solubility.

[0066]

Gallic acid and tannic acid of compounds having aromatic benzene-rings, oxidation inhibitors, may be used as other anti-corrosive agents. These additive rates are preferably made 0.01 to 5% in the same light as the anti-corrosive agent like BTA.

[0067]

In the present embodiment, it was confirmed that an anti-corrosive film is formed on a Cu-interconnection surface as with the first embodiment. Additionally, in accordance with the present embodiment, adhesion between Cu and the Cu-diffusion stopper insulating film may be improved without having to increase the number of processes.

[0068]

[Effects of the Invention]

As has been described hereinbefore, the present invention has enabled to improve the adhesion between the metal interconnection and the Cu-diffusion stopper insulating film in the semiconductor device which forms the Cu-diffusion stopper insulating film on a surface of the damascene Cu-

interconnection comprising Cu or a Cu-alloy. The present invention has also enabled to provide the highly reliable semiconductor device, because no hillock is formed on the metal interconnection surface.

[0069]

The anti-corrosion treatment according to the present invention, which uses a low dielectric constant film (Low-K) as an inter-layer insulating film, is important particularly in case that the Cu-interconnection is formed in this Low-K film. Generally, in accordance with conventional methods, the Low-K film is likely to contain moisture as compared to a SiO_2 film. Thus, this moisture affects the Cu-interconnection, leading to easier oxidation of the Cu-interconnection. However, in accordance with a method of the invention of the present application, excellent adhesion between the Cu-interconnection and the Si_3N_4 film prevents entry of the moisture, and further the Cu-interconnection surface subjected to the anti-corrosion treatment prevents oxidation thereof, even with the entry of the moisture.

[Brief Description of the Drawings]

[FIG. 1]

A process chart showing a method of manufacturing a semiconductor device according to a first embodiment of the present invention.

[FIG. 2]

Graphs showing measurement results of TOF-SIMS on CuO.

[FIG. 3]

A graph showing the measurement results of the TOF-SIMS on organic substances.

[FIG. 4]

A graph showing the measurement results of the TOF-SIMS on Cu-BTA.

[FIG. 5]

A diagram showing the measurement results of sheet resistance.

[FIG. 6]

A process chart showing a method of manufacturing the semiconductor device according to a second embodiment of the present invention.

[FIG. 7]

A process chart showing a process of manufacturing a conventional

semiconductor device for making a damascene Cu-interconnection.
[FIG. 8]
Fragmentary cross sectional elevation views of the semiconductor wafer in a manufacturing process thereof.
[Explanation of the Reference Numerals]
10 SEMICONDUCTOR SUBSTRATE
12 INSULATING FILM
14 BARRIER METAL LAYER
15 Cu FILM
16 PLATED Cu
17 Cu-INTERCONNECTION
18 Si_3N_4 FILM
19 INTER-LAYER FILM
20 Cu-CMP PROCESS
22 SCRUB CLEANING PROCESS
24 SPIN CLEANING PROCESS
26 SPIN-RINSE + DRY PROCESS
28 FILM FORMING PROCESS
29 INTER-LAYER FILM FORMING PROCESS
30 (SPIN CLEANING + ANTI-CORROSION TREATMENT) PROCESS

[Document Type] Abstract
[Abstract]
[Problem to be solved] To provide a method of manufacturing a semiconductor device which solves a problem with poor adhesion between a metal interconnection including copper or a copper alloy and a copper-diffusion stopper insulating film, and which prevents formation of a hillock.
[Solution] After cleaning a copper surface in a spin cleaning process 24 before treating a wafer surface in an anti-corrosion treatment process 25, a surface of a Cu-interconnection 17 is subjected to the anti-corrosion treatment. As an anti-corrosive solution, a BTA solution having an addition of 1% BTA is prepared. A semiconductor wafer is rotated with supply of the BTA solution to the wafer surface at a flow rate of 1 liter/min. for 10 seconds to carry out Cu-film anti-corrosion. The surface of the Cu-interconnection is

prevented from oxidation even with exposure to the atmosphere, because Cu-BTA compounds are formed on the surface of the Cu-interconnection 17 as an anti-corrosive film. This provides excellent adhesion of an interface between Cu and Si_3N_4 even if an Si_3N_4 film is then formed.
[Selected Drawing] FIG. 1

Fig. 1

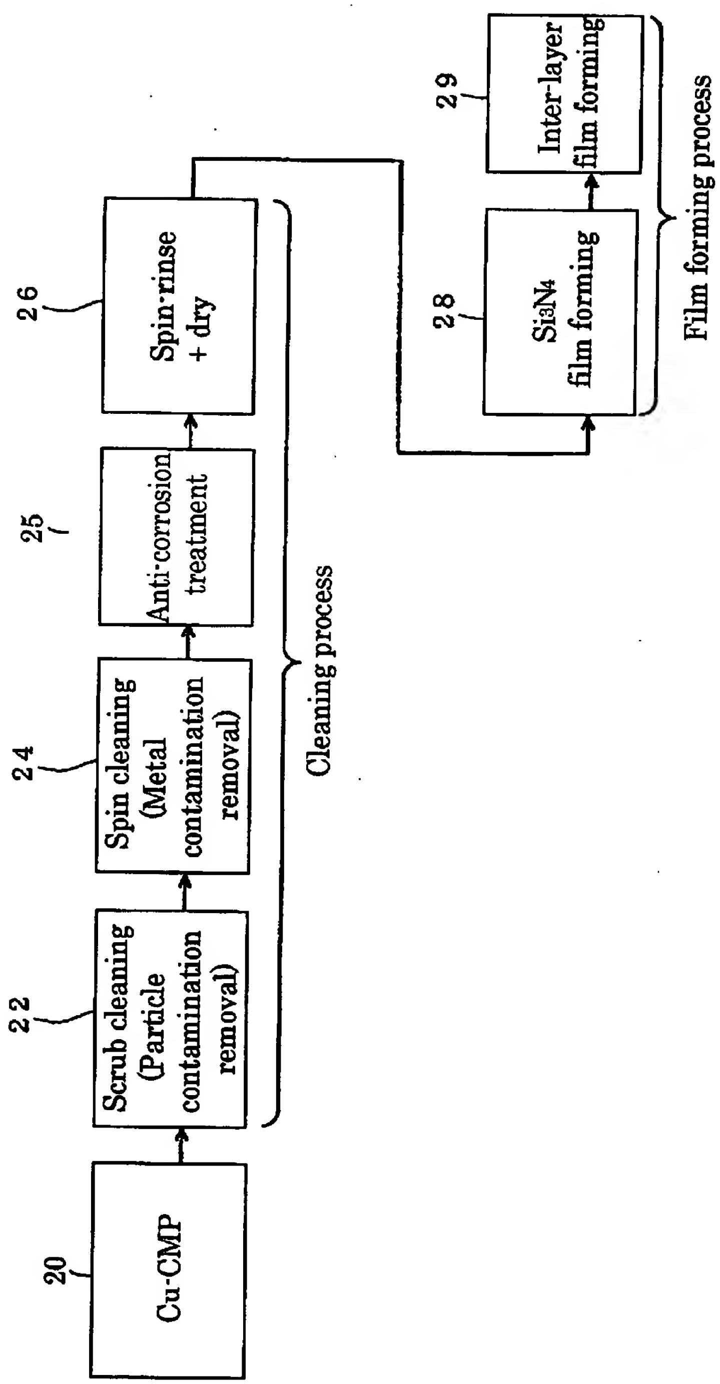
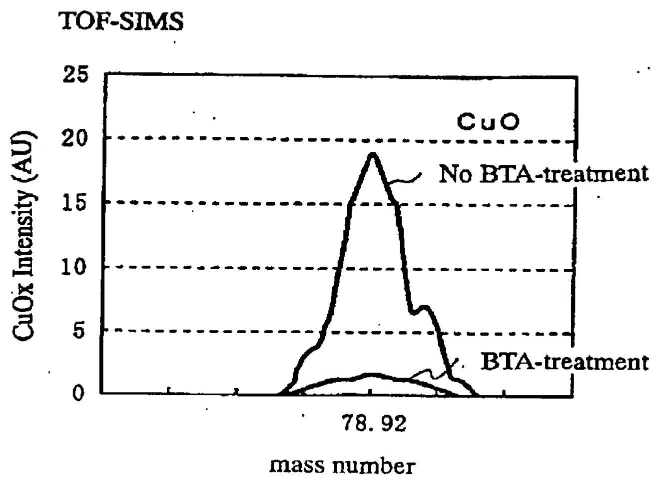

20
Cu-CMP
22
Scrub cleaning (Particle contamination removal)
24
Spin cleaning (Metal contamination removal)
25
Anti-corrosion treatment
26
Spin·rinse + dry
Cleaning process
28
Si_3N_4 film forming
29
Inter-layer film forming
Film forming process

Fig. 2

(A)


TOF-SIMS
CuOx Intensity (AU)
25
20
15
10
5
0
CuO
No BTA-treatment
BTA-treatment
78.92
mass number

(B)

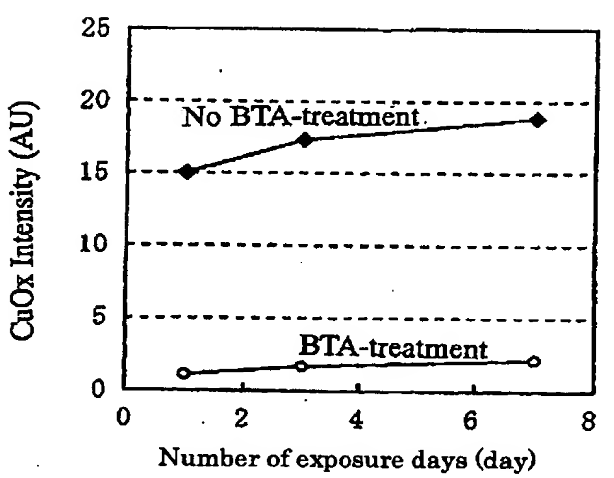

CuOx Intensity (AU)
25
20
15
10
5
0
No BTA-treatment
BTA-treatment
0
2
4
6
8
Number of exposure days (day)

Fig. 3

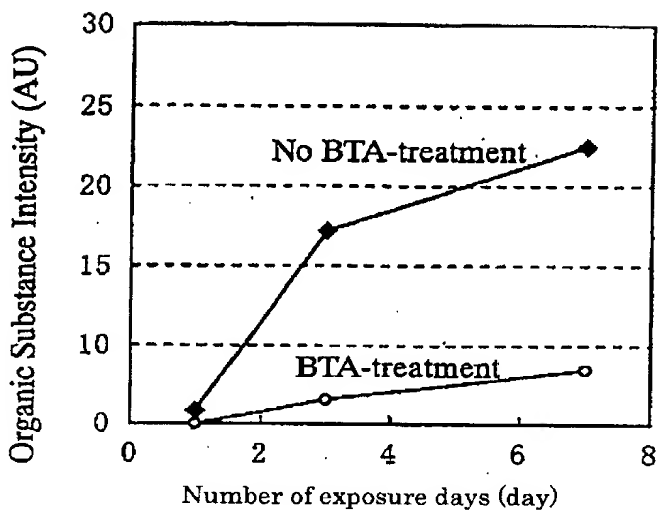

30
25
20
15
10
0
Organic Substance Intensity (AU)
No BTA-treatment
BTA-treatment
0
2
4
6
8
Number of exposure days (day)

Fig. 4

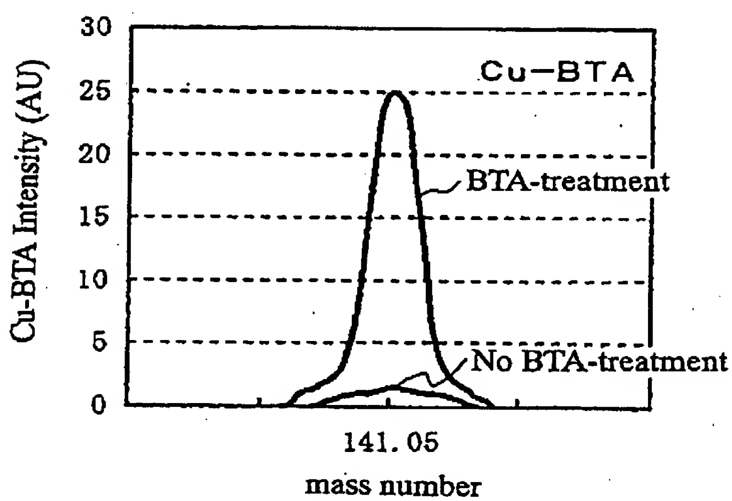
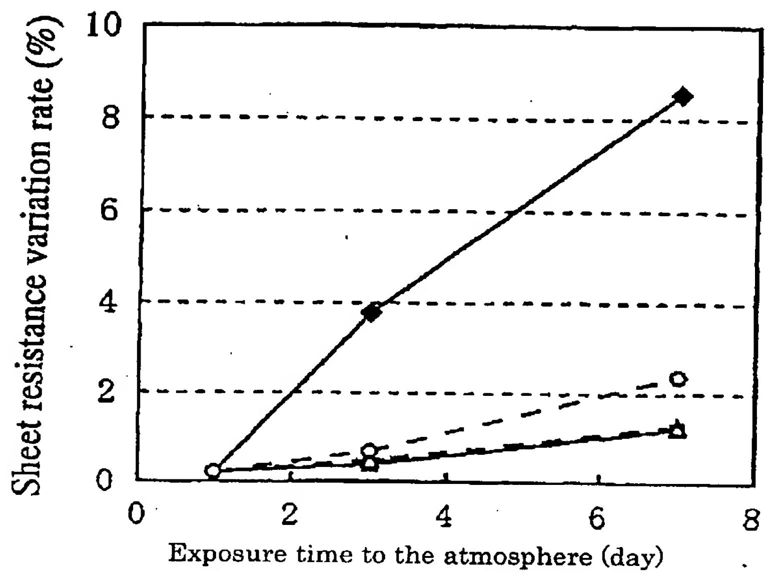

30
25
20
15
10
5
0
Cu-BTA Intensity (AU)
Cu−BTA
BTA-treatment
No BTA-treatment
141.05
mass number

Fig. 5



◆: the semiconductor wafer free from the benzotriazole treatment

■: the semiconductor wafer treated with the 0.1%-benzotriazole solution

△: the semiconductor wafer treated with the 1%-benzotriazole solution

○: the semiconductor wafer treated with the 1%-gallic acid solution

Fig. 6

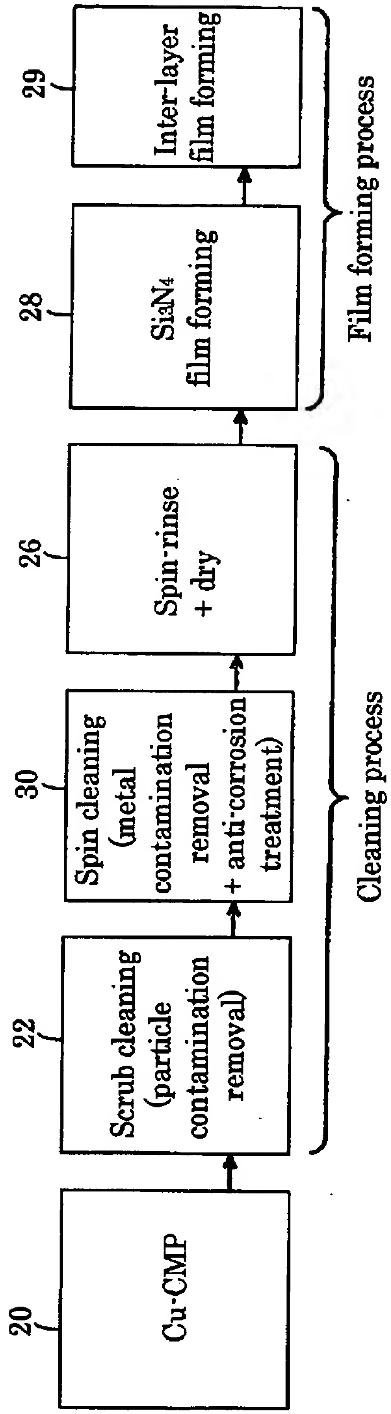

20
Cu·CMP
22
Scrub cleaning (particle contamination removal)
30
Spin cleaning (metal contamination removal + anti·corrosion treatment)
26
Spin·rinse + dry
28
Si3N4 film forming
29
Inter-layer film forming
Cleaning process
Film forming process

Fig. 7

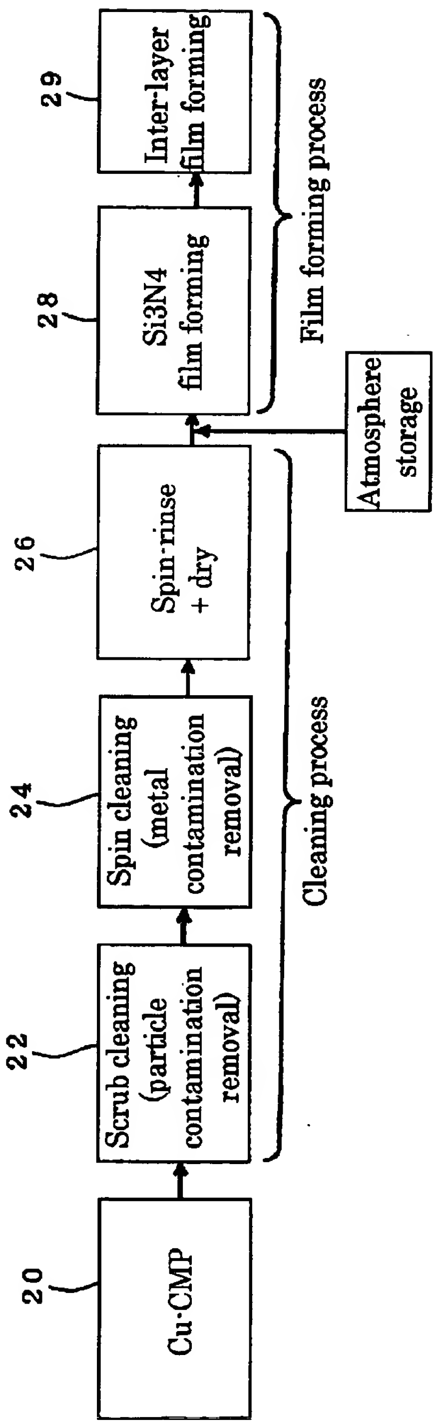

20
Cu·CMP
22
Scrub cleaning (particle contamination removal)
24
Spin cleaning (metal contamination removal)
26
Spin-rinse + dry
28
Si3N4 film forming
29
Inter-layer film forming
Atmosphere storage
Cleaning process
Film forming process

Fig. 8

(A)

(B)

(C)